(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 355 228 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 88307855.2

(51) Int. Cl.4: C11D 3/386

(22) Date of filing: 24.08.88

(43) Date of publication of application:
28.02.90 Bulletin 90/09

(84) Designated Contracting States:
BE DE ES FR GB IT LU NL SE

(71) Applicant: TUKOVY PRUMYSL, KONCERN
Opletalova 4
Praha 1(CS)

(72) Inventor: Novak, Jan,Csc
Pod Vaclavem 2052
Rakovnik(CS)
Inventor: Kralova, Blanka, Csc.
Leninova 674
Praha 7(CS)
Inventor: Demnerova, Katerina, Doc. Ing.
Obrancu miru 63
Praha 7(CS)
Inventor: Prochazka, Karel
Pod Vaclavem 2051
Rakovnik(CS)
Inventor: Vodrazka, Zdenek, Prof. Dr. Ing.
U smaltovny 19
Praha 7(CS)
Inventor: Tolman, Jiri
Roztoky 137
Krivoklat(CS)
Inventor: Rysava, Dana
Kyjevska 280
Jindrichuv Hradec(CS)
Inventor: Smidrkal, Jan, Csc.
Husovo namesti 115
Rakovnik(CS)
Inventor: Lopata, Vaclav
Brigady 1845
Rakovnik(CS)
Inventor: Kovar, Pavel
Pod stadiony 21
Praha 5(CS)
Inventor: Soucek, Jiri
Plzenska 203
Praha 5(CS)

(74) Representative: Griffin, Kenneth David et al
Saunders & Dolleymore 9, Rickmansworth Road
Watford Hertfordshire WD1 7HE(GB)

(54) Enzymic agent for washing, degreasing and water reconditioning.

(57) The detergent is based on an enzyme complex, and particularly on lipases and oxidoreductases. A substantially lower contents of surfactants and chelatizing components positively influences the effects of enzyme constituents on all of the basic dirt types, except for pigments, and promotes the environmental protection. Apart from this, the washing ability of this detergent even if used at low temperatures has its significance in power econonmy.

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ENZYMIC AGENT FOR WASHING, DEGREASING AND WATER RECONDITIONING

The invention relates to an enzymic agent for washing, degreasing, cleaning and reconditioning of polluted and waste water, the agent being capable of degrading hydrophobic chains having from 5 to 35 carbon atoms.

The present level of washing and cleaning agents is practically balanced all over the world. A relatively high effectiveness is attained by their composition which, with small modifications, has been established on using combinations of anionic and nonionic surfactants, chelatizing substances and specific admixtures among which the most significant detergent effect is based on proteinases and amylases, sodium perborate, carboxymethylcellulose and optical brighteners.

To achieve the desired utility properties, it is in most cases necessary to use the mechanical effect of heating. Especially the removal of a high content of hydrophobic substances requires power, surfactant and alkali contents. If in washing the afore-mentioned requirements are not met, fatty dirt may precipitate to hardly seperable particles. The detergence process gives rise to relatively high waste water volume on the reconditioning of which, and particularly the separation of surfactants and builders, considerable costs have to be expended.

Apart from this, the disemulsification of hydrophic substances is usually very demanding, since it requires the addition of other ingredients, special plants and, in general, is cause of increasing costs on the waste water reconditioning.

As known, among the raw materials used at present in detergents, cleaning and like agents, proteases and amylases do not require energy and investments for protecting the purity of environment. In spite of this fact there are concerned highly effective components which, in general, reduce requirements on power needed for the separation of both proteinaceous and polysaccharidic impurity components. However, these enzymes are of a highly selective nature and are far from removing all of the dirt constituents, and particularly their hydrophobic part which has hitherto been separable by the application of surfactants. Nevertheless after the washing process the problem of disposing of the used surfactants and the released hydrophobic substances has to be solved.

In order to eliminate the drawbacks of prior art as hereinabove set forth, the invention provides an improved enzymic agent for washing degreasing, cleaning both moisture-adsorptive and non-adsoptive materials, and for reconditioning polluted and waste water, the agent containing activating, softening, surface active, filling, perfuming, colouring, proteolytic, amylolytic and buffering admixtures or combinations thereof, and consisting, according to the invention, in that it contains from 0.1 to to 50 % by weight, preferably, from 0.5 to 10 % by weight of a multi-enzyme complex based on lipases and oxidoreductases whose minimum lipase activity is 2 units per mg of protein, and oxidoreductase activity of alkanehydroxylase is at least 0.5 nkat per mg of protein, and that of alcoholdehydrogenase is 0.5 unit per mg protein, the agent comprising further from 2 to 45 % by weight of nonionic and/or anionic surfactants while the remainder, up to 100 %, is formed by chelatizing, filling, colouring, perfuming, brightening, biological and other admixtures.

By an agent according to the invention, hydrophobic substances can be removed by using substantially smaller amounts of surfactants, or dispense with them entirely, which, from ecological viewpoint, has an extraordinary significance. Further the agent makes it possible to raise the effectiveness of existing washing and cleaning agents in that they can be used at lower temperatures, which also means considerable power savings.

The agent according to the present invention is capable of successfully dissolving impurities whose hydrophobic part contains chains of hydrocarbons, alcohols, organic acids and derivatives thereof having from 5 to 35 carbon atoms.

The conversion of all the above-mentioned substances to shorter, water-soluble and biologically easily degradable ones, such as acetic and propionic acids, is provided for by the enzyme complex with lipase, alkaneoxidase and alcohol-dehydrogenase activities. In the sequence of enzyme reactions lipases are active as the first, and split, in the presence of higher fatty acid esters of alcohols, the ester bond; thus, for instance, fatty acids and alcohols are degraded by a system of oxidizing reactions, and particularly by oxidation. Also aliphatic hydrocarbons are degraded by a multi-stage oxidation which, as a rule, is initiated by hydroxylation of carbon atom C_1 whereby first alcohol, and in the next stage an acid is produced. This stage is followed by oxidation, ie acetyl, or propionyl Co A are degraded in the citrate or methylcitrate cycle whereby carbon dioxide and water is obtained.

The use of enzyme system in washing, cleaning and degreasing agents makes it possible to raise detergence effectiveness with the existing but also even substantially lower surfactant and chelatizing

substance contents, to extend the complex effectiveness of enzyme components to all the fundamental impurity components, except pigments, and to promote easier protection of environment.

An agent according to the invention and its effects are illustrated with the help of the following examples. There was always concerned a series of experiments which were effected in order to document the influence of the concentration used, and differently active multi-enzyme complexes on the increase of washing ability if compared with a reference (examples 5 and 6) or the influence of temperature on washing ability (example 4). Another series of examples 1, 2 and 3 illustrates a higher washing ability of agents on the basis of surfactants and of the multi-enzyme complex in relation to the surfactants themselves, and further proves that an increase of washing ability because of the use of multi-enzyme complexes relative to a reference is not influenced by the use of various surfactant types and change of concentrations thereof, either. Since the individual series of experiments were effected in successive time intervals, various types of textile fabrics were used therefor, and this influences, to some extent, the absolute values of the resultant washing ability.

EXAMPLE 1.

5 grams of a detergent composed of 25 % by weight of tripolyphosphate, 2 % by weight of lauryl polyglycol ether, containing 12 moles of ethyloxide, 4 % by weight of multi-enzyme agent with an intensified lipase activity of the complex of 20 units/mg protein, alkanehydroxylase activity of 0.6 nkat/mg of protein, and alcoholdehydrogenase activity of 1.5 unit/mg of protein, and a variable amount of sodium dodecylbenzene sulphonate, made up to 100 % by weight with water, were dissolved and made up to one litre volume with water containing 5.34 mmol of Ca^{2+}/litre. The thus obtained solution was used for a test of washing cotton cloth soiled with standard dirt, at 40 °C for 15 minutes in a laboratory washing machine of the LIMITEST type. Results of the washing ability test on the detergent, in dependence upon the weight per cent contents of dodecylbenzene sulphonate (DBS), are tabulated in the following Table I.

TABLE I

Dodecylbenzene sulphonate (DBS) (%)	Washing ability without enzymes	Washing ability with enzyme multi-complex
0	40.6	47.3
3	53.1	60.4
6	57.6	64.2
9	58.8	66.0
12	69.2	80.0

EXAMPLE 2

The amount of 5 grams of a detergent composed of 6 % by weight of sodium alkylbezene sulphonate, 2 % by weight of laurylpolyglykaoether containing 12 moles of ethyloxide, 3 % by weight of a multi-enzyme complex with lipase activity of 10 units/mg of protein and with intensified oxidoreductase activity with alkanehydroxylase activity of 1.5 nkat/mg or protein and alcoholdehydogenase activity of 1.5 unit/mg, with a variable amount of sodium tripolyphosphate, made up to 100 % by weight with water, were dissolved and made up to one litre volume with water, containing 5.34 mmol Ca^{2+} per litre. The obtained solution was used for a test of washing cotton cloth soiled with standard dirt, at 40 °C for 15 minutes in a laboratory washing machine. Results of the washing ability test, in dependence upon the content of sodium tripolyphosphate (TPP) are tabulated in the following Table II:

TABLE II

TPP (% by weight)	Washing ability without enzymes	Washing ability with multi-enzyme complex
0	5.0	12.5
5	56.4	65.7
10	58.9	66.9
15	61.7	67.2
20	62.4	69.1
25	63.2	70.1

EXAMPLE 3

The amount of 5 grams of a detergent composed of 2 % by weight of lauryl polyglycol ether containing 12 moles of ethyl oxide, 3 % by weight of a multi-enzyme complex intensified both oxidoreductase and lipase activities as in Example 2, with a variable amount of sodium tripolyphosphate, made up to 110 % by weight with water, were dissolved and made up with water containing 45.34 mmol Ca^{2+} per litre to one litre volume. The obtained solution was used for a test for washing cotton cloth soiled with standard dirt, at 40 °C for 15 minutes in a laboratory washing machine LIMITEST. Results of the washing ability test of the detergent, in dependence upon the sodium tripolyphosphate content, are listed in the following Table III:

TABLE III

TPP (% by weight)	Washing ability without enzymes	Washing ability with multi-enzyme complex
0	1.0	3.9
5	33.9	41.9
10	34.2	41.9
15	39.8	45.7
20	38.9	46.7
25	40.3	47.0

EXAMPLE 4

To 1000 ml of a buffer phosphate solution with pH-value of 8 were added 5 grams of a washing agent constituted only be 100 % by weight of a multi-enzyme complex with intensified oxidoreductase activity as in Example 2. The obtained solution was used for a test of washing cotton cloth soiled with standard dirt, for 15 minutes under laboratory conditions at a variable temperature. The results of the washing ability test are tabulated in the following Table IV:

TABLE IV

Temperature (°C)	Washing ability without enzyme	Washing ability with multi-enzyme complex
30	12.4	18.0
37	17.9	26.9
50	30.1	45.9

EXAMPLE 5

To 1000 ml of buffer phosphate solution (pH 8) were added from 0.2 to 5 grams of a washing agent containing only 100 % by weight of a multi-enzyme complex with lipase activity and intensified oxidoreductase activity as in Example 2. The obtained solution was used for a test of washing cotton cloth soiled with Czechoslovak standard dirt, under laboratory conditions at 50 °C for 15 minutes. The results of the washing ability test in dependence upon the amount of multi-enzyme complex, are tabulated in the following Table V:

TABLE V

Multi-enzyme complex (gram/litre)	Washing ability specimen	Washing ability (reference without enzyme)
0.2	45	32
0.5	48	34
1.0	48	32.5
2.0	51	34
3.0	53	33.5
4.0	53	35
5.0	55	35.9

EXAMPLE 6

To 1000 ml of a phosphate buffer (pH 8) was added a variable amount of from 0.2 to 5 grams of a washing agent containing only 100 % by weight of a multi-enzyme complex with oxidoreductase activity and intensified lipase activity as in Example 1. The obtained solution was used for a test of washing cotton cloth soiled with Czechoslovak standard dirt, under laboratory conditions at 50 °C for 15 minutes. For results of washing ability tests depending on the amount of multi-enzyme complex see the following Table VI:

TABLE VI

Multi-enzyme complex (gram/litre)	Washing ability specimen	Washing ability (reference without enzyme)
0.2	32.5	23.8
0.5	31.8	24.5
1.0	33.5	23.5
2.0	37.3	27.3
3.0	35.5	25.3
4.0	34.3	21.3
5.0	31.6	18.0

EXAMPLE 7

In a conventional process of producing pulverized agents there was prepared mixture of 7 % by weight of dodecylbenzene sulphonate, 3 % by weight of nonyl polyglycol ether, 20 % by weight of tripolyphosphate, 1.5 % by weight of carboxymethylcellulose, 3 % by weight of sodium silicate, 0.2 % by weight of an optical brightener, 3 % by weight of amophous silicic acid, 0.2 % by weight of a pefume, 2 % by weight of a multi-enzyme complex capable of degrading hydrophobic chains with 5 to 35 carbon atoms and exhibiting an intensified lipase activity (in capsulated form) as in Example 1, and 60.1 % by weight of sodium sulphate. When compared with a reference specimen without multi-enzyme complex there was reached, within the entire range of evaluated concentrations is dependence on the temperature of from 30 to 50 °C an increase of luminance factor by seven units.

EXAMPLE 8

A washing and degreasing agent with a 20 % surfactant content (ammonium alkylbenzoate, sodium polyglycolether) and ammonium laurylsulphate -3:1:1 by weight) was compared with a solution of multi-enzyme complex capable of degrading hydrophobic chains with 5 to 35 carbon atoms, in the concentration of 0.02 gram/litre in phosphate buffer solution (pH 8). The multi-enzyme complex had the following activities: Lipase - 2 units/mg of protein; alkanehydroxylase - 0.5 nkat/mg; and alcoholdehydrogenase - 0.5 unit/mg of protein. The comparison was affected on a glass fibre cloth containing paraffins and triglycerides. The values achieved at a temperature of from 40 to 50 °C within a period of from 30 to 60 minutes in the LIMITEST machine turned out to be identical.

EXAMPLE 9

A liquid degreasing agent had the following composition:
40 % by weight of ethoxylated alcohols C_{10-14} with epoxy groups;
20 % by weight of multi-enzyme complex with lipase activity of 2 units/mg of protein, and alcohol-dehydrogenase activity of 0.5 unit/mg of protein; and alkanehydroxylase activity of 0.5 nkat/mg;
2 % by weight of sodium humenesulphonate; and
38% by weight of water.

EXAMPLE 10

A washing and degreasing pulverized agent had the following composition:
50 % by weight of multi-enzyme complex from Example 9;
5 % by weight of sodium alkylbenzene sulphonate;
5 % by weight of soda soap;
2 % by weight of ethylene oxide/propylene oxide copolymer;
20 % by weight of synthetic zeolite;
15 % by weight of sodium tripolyphosphate;
1.4 % by weight of sodium sulphate;
0.3 % by weight of optical brighteners;
0.3 % by weight of perfume; and
1.0 % by weight caroxymethylcellulose.

EXAMPLE 11

A washing powder had the following composition:
5 % by weight of sodium alkylbenzene sulphonate;
5 % by weight of soda soap;
3 % by weight of ethylene oxide/propylene oxide copolymer;
1 % by weight of proteinase;
1 % by weight of amylase;
1 % by weight of multi-enzyme complex as in Example 2;
20 % by weight of zeolite;

20 % by weight of tripolyphosphate;
0.3 % by weight of optical brighteners;
0.3 % by weight of perfume;
1.0 % by weight carboxymethylcelluiose;
1.4 % by weight of sodium silicate;
41 % by weight of sodium sulphate.

Claims

1. An enzymic agent for washing, degreasing, cleaning both moisture-adsoptive and non-adsorptive materials and for reconditioning polluted and waste water, characterised in that it contains from 0.1 to 50 % by weight of a multi-enzyme complex based on lipases and oxidoreductases whose minimum lipase activity is 2 units per mg of protein, and oxidoreductase activity of alkanehydroxylase is at least 0.5 nkat per mg of protein, and alcohol-dehydrogenase activity is 0.5 unit per mg protein, the agent comprising further from 2 to 45 % by weight of non-ionic and/or anionic surfactant while the remainder, up to 100 %, is formed by chelatizing, filling, colouring, perfuming, brightening, biological and other admixtures.

2. An enzymatic agent according to Claim 1 characterized in that it contains from 0.5 to 10 % by weight of said multi-enzyme complex.

3. An enzymatic agent according to any one of the preceding claims characterized in that the lipase activity is between 2 and 20 units per mg of protein.

4. An enzymatic agent according to any one of the preceding claims characterized in that the oxidoreductase activity of alkalenehydtoxylase is between 0.5 and 1. 5 nkat per mg of protein.

5. An enzymatic agent according to any one of the preceding claims characterized in that the alcohol-dehydrogenase activity is between o.5 and 1.5 units per mg protein.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 30 7855

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	EP-A-0 019 315 (PROCTER & GAMBLE) * Claims 1,12 *		C 11 D 3/386

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 11 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14-03-1989	PFANNENSTEIN H.F.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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